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Carbon sequestration and the role of biological carbon mitigation: A review

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ABSTRACT

Climate change and rising atmospheric CO_2 levels have become much debated environmental issues in recent years. Point source emissions of CO_2 from industrialised processes such as power generation and cement production account for much of this increase. Direct carbon sequestration and storage techniques such as geological injection have large storage capacities, however these methods are very cost inefficient and have not been proved safe for long term sequestration. A novel approach to offsetting emissions is through direct biological carbon mitigation where CO_2 from the flue gases of point sources is used to cultivate photosynthetic autotrophic organisms. The produced biomass can subsequently be converted into biofuels, bio-chemicals, food or animal feed. These useful by-products provide revenue to finance the carbon mitigation process. Large-scale cultivation of biological media on site at a power generation plant means that substantial amounts of biomass could be readily available for co-firing in the plant, thus decreasing the demand for fossil fuels. This review gives an overview of the most suitable strains of microalgae for the purpose of carbon mitigation while the challenges associated with carbon mitigation strategies such as capital costs, environmental issues, and cultivation of microalgae using flue gases will also be assessed. Selected media will be required to have a high CO_2 fixing rate, a rapid growth rate, while being easily cultivated on a large scale in order to generate a large biomass yield and produce valuable by-products to offset the costs of carbon mitigation. An economic balance is also discussed to give an indication of the cost benefits in the implementation of biological carbon mitigation policies as a solution to the high capital and running costs of large scale microalgal production.

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1. Introduction

Concerns over global warming and carbon emissions have sparked interest in methods of sequestering carbon which has been released through the burning of fossil fuels. Human activity is already directly and indirectly affecting almost half of the terrestrial biological carbon cycle [1]. If this cycle were properly managed, it could be a major contributor to the mitigation of CO_2 [1]. A large fraction of the anthropogenic carbon dioxide (CO_2) emissions results from the combustion of fossil fuels for energy production. With energy needs increasing, especially in the emerging economies of the developing world, CO_2 emissions are expected to rise considerably in the coming years [2]. It has been widely recognised that high levels of CO_2 in the atmosphere has some detrimental effects on the environment [2–4]. Increased atmospheric CO_2 levels are a positive driver of the greenhouse effect causing atmospheric temperatures to rise as shown by Soon et al. [4]. This leads to the melting of polar ice, rising sea levels, climate change and extreme weather conditions. With small increases in atmospheric CO_2, soil and vegetation carbon will increase due to enhanced growth rates. However growth is inhibited at higher levels of atmospheric CO_2 as photosynthesis will reach a maximum level while soil respiration rate will increase with temperature further increasing atmospheric CO_2 levels [5,6]. The ocean absorbs over 25% of the annual release of anthropogenic CO_2 [7]. This makes it the principal natural carbon sink for emitted CO_2. But this atmospheric environmental benefit comes at a price. Increased levels of CO_2 in sea water leads to the formation of carbonic acid. This process, known as ocean acidification, has led to a 30% increase in ocean acidity since the beginning of the industrial revolution [7]. The increase in water acidity decreases the ability of marine organisms to build shells and skeletal structure [7]. An increase in ocean acidification would principally affect non-swimming marine organisms, such as zooplankton, bacteria and benthos, at depths of 1000 m or more [6]. Though the long term effects are not fully understood, it is believed that further increases in ocean acidity will lead to the demise of marine life [5,7]. Meeting energy demands without high emissions will require stringent management of CO_2 including the use of post combustion carbon sequestration. Direct carbon capture and sequestration is a process of removing CO_2 from flue gases and storing it for extended periods, preventing emissions. It has been defined as the deliberate human-controlled separation of CO_2 from other by-products of combustion and transfer to some non-atmospheric reservoir for permanent or quasi-permanent storage [8]. Conversely, indirect carbon sequestration has been defined as that which does not require human controlled manipulation of CO_2; instead, natural processes, such as the uptake of CO_2 by living organisms, are fostered so as to accumulate CO_2 at a greater rate than would otherwise have occurred [8]. Biological carbon mitigation (BCM) is the process whereby autotrophic organisms and plants convert this CO_2 into organic carbon through photosynthesis producing large amounts of biomass [9]. All biological media contain carbon and the major stores of carbon can be found in vegetation (e.g., forestry), soils (e.g., peat), as well as a large portion being sequestered over time naturally in the ocean [3,10–12]. Through photosynthesis and other metabolic pathways, carbon becomes incorporated into the cells of these organisms [9,13]. Careful management of the carbon cycle would ensure that biomass could be utilised for various commercial applications while ensuring sufficient carbon is stored in biological media, thereby maintaining safe levels of CO_2 in the atmosphere [14]. Produced biomass could be used in applications including; biofuel production, food, feeds, and biochemical production [15]. In biofuel production the CO_2 is essentially being recycled, while the use of biomass in the "biomass-to-energy" chain displaces the use of fossil fuels for energy production [16]. Photosynthesis is the process by which certain organisms utilise anthropogenic carbon to produce biomass and was the original process that fixed carbon millions of years ago creating today's fossil fuels [17]. Using this process captured flue gases containing high concentrations of CO_2 can be used to cultivate large amounts of biological media. In a controlled environment, this will produce large yields of valuable biomass for producing biofuels, as well as some value added by-products [15]. Selection of the most suitable media for carbon sequestration is crucial in achieving a high level of CO_2 removal while also ensuring maximum economic gain from the process [17]. In this paper, the potential of microalgae to mitigate large amounts of anthropogenic carbon from point sources will be assessed. The objective of this paper is to provide a holistic detailed overview of the process of direct and indirect carbon sequestration and in particular the role of BCM. The legislative and policy drivers of direct BCM are examined as well as the issues associated with CO_2 recovery from point sources. Suitable media for BCM are examined while the ability of microalgae to successfully mitigate CO_2 from point sources is discussed in detail. The commercial applications of produced biomass from microalgae are assessed to determine the fate of mitigated carbon as well as the cost-effectiveness of BCM using microalgae. This paper also discusses the technical barriers including environmental concerns and economic matters to be overcome to allow for widespread implementation of the practise of direct BCM.

2. Legislative and policy drivers of direct biological carbon mitigation

Currently there is a lack of government policies which support the practise of direct BCM from fossil fuel point source CO_2 emitters, as carbon sequestration. Consequently if biological carbon mitigation is exercised at fossil fuel point source CO_2 emitters, abatement of released CO_2 has to be considered in the context of continued fossil fuel usage [16]. However, much attention is currently being directed to a range of international and domestic policy actions to reduce CO_2 emissions due to their potentially damaging effects on the environment [18]. CO_2 emission rates depend on world economic activity, the energy efficiency of a particular process, and the carbon content of the source of CO_2 emissions [18]. The Kyoto protocol requires countries to reduce CO_2 emissions. Under this agreement Annex 1 countries may reduce emissions by decreasing fossil fuel consumption or by increasing net carbon sequestration in terrestrial carbon sinks [14]. Other policies that have been proposed to reduce CO_2 emissions include research and development funding, tax credits, energy efficiency standards, and CO_2 cap-and-trade systems [18]. Relevant national and international policies may need to be altered if direct BCM is to achieve widespread implementation. Biofuels for example were initially utilised to reduce dependence on oil but by the 1990s environmental concerns, with excessive emissions from fossil fuels, became more influential and the introduction of the carbon tax in 1991 aided the economic potential of biofuels [19]. The power of government policy on the use of low carbon fuel sources is evident in Finland and Sweden where the introduction of high carbon taxes has led to a high renewable energy market share in most notably the use of biofuels for transport [20]. Jaffe et al. [21] found that many economists agreed that the ‘polluter pays principles’, where polluting goods are taxed, are more effective at reducing emissions than subsidies for non-polluting alternatives. Based on this principle, carbon taxes on excessive emissions are considered more effective to avert emissions than subsidies on biofuel production [20,21]. However, while taxes increase government revenues, it can have an effect on the price of consumer goods as well as producer surplus depending on the elasticity of the product [20]. In a study by Morgerstern et al. it was found that within the manufacturing sector only a small number of industries would bear a disproportionate burden of a carbon mitigation policy [22]. It was also found that some of or the entire burden was likely to be passed on to customers. Therefore, the ‘*who pays*’ issue may be more accurately described as who pays initially as most of the burden is most likely being passed on to consumers [22]. In this scenario, policy will need to be implemented which will ensure that the cost of carbon mitigation will be distributed across a range of areas so as to avoid the concentration of costs on a small number industries or individuals [22]. The International Energy Agency predicts that global energy related emissions of CO_2 will reach 38 billion tonnes per annum in 2030, which is 70% above 2002 levels, with two-thirds of the increase expected to come from developing countries [23]. Policies of the Organisation for Economic Co-operation and Development (OECD) aim to curb energy demand and emissions by switching to less carbon intensive fuels i.e., revert to renewables in energy production [23]. The IEA developed an OECD Alternative Policy Scenario to assess the impact of various government policies and industrial technological advances on the energy supply and demand with the aim of reducing emissions of the OECD countries by some 2150 Mt or 16% below the reference scenario in 2030 [23]. This is said to be achievable through the use of low carbon fuels in energy production, i.e., switching from coal to natural gas, and increasing the use of renewables [23]. The report also states that carbon sequestration and storage technologies hold long term prospects in creating zero emission energy production, but that the technologies are unlikely to be deployed on a large scale before 2030 due to the high cost and lack of development of technology in the area [23]. The IEA World Energy Outlook 2012 presents an Energy Development Index which is a composite index measuring the energy development of over 80 countries. The aim of this index is to assist policy makers in tracking progress of these countries towards providing modern energy access [24]. The report aims to promote sustainable energy policies that aim to spur economic growth and protect the environment through the reduction of GHG emissions [24]. However, the report also states that taking all new developments and policies into account that the world is still failing to put the global energy system onto a more sustainable path [24]. The IEA aims to limit global warming to 2 °C but show that this becomes more difficult with each year that passes [24]. To achieve this goal no more than one-third of current proven reserves of fossil fuels can be consumed prior to 2050 unless carbon capture and storage technology becomes widely deployed [24]. With increasing fossil fuel prices, carbon capture and the use of renewables in energy production becomes much more economically viable [24]. In contrast to the IEA predictions Caldeira et al. observed that to achieve the 2 °C global average temperature increase we would need to install $\sim 900 \pm 500$ MW of carbon emissions-free power generating capacity each day over the next 50 years which equates to one large emission free power plant coming into use every day between now and then [25]. This advocates the need for carbon mitigation and storage as this is a feasible strategy for the reduction of emissions and planetary rescue [26,27]. Establishing the need for policy and legislation with regard to carbon mitigation is important but the need for experimental data on the ability of carbon mitigation strategies to effectively reduce emissions is required by policy makers. With regard to microalgae there is currently work being done by EnAlgae on the collection of data for use by policy makers [28]. EnAlgae is a four-year strategic initiative of the INTERREG IVB North West Europe programme which brings together 19 partners and 14 observers across 7 EU Member States with the aim of developing sustainable technologies for algal biomass production [28]. One work package aims to identify political, economic, social and technological opportunities which promote the adoption of algal biomass within North West Europe [28]. This work is expected to assist policy makers, industry and investors in understanding which algal production systems, standards and markets are applicable to the region [28]. More funding will need to be directed to projects such as EnAlgae so that policy makers may put legislation in place which promotes CSS in an economical and environmentally fair manner. The Intergovernmental Panel on Climate Change (IPCC) Special Report on Carbon Dioxide Capture and Storage (SPCSS) provides information for policymakers, scientists and engineers in the field of climate change and reduction of CO_2 emissions [29]. It describes sources, capture, transport, storage costs, economic potential of CO_2 as well as the environmental and public health issues of the technology [29]. The report shows the need for legislation by indicating that few countries have specifically developed legal or regulatory frameworks for long-term CO_2 storage. This means that carbon mitigation schemes are unlikely to be deployed on a large scale in the absence of explicit policy that limits atmospheric emissions [29]. BCM offers great potential for diverting anthropogenic GHGs from the atmosphere and, depending on the utilisation of produced biomass, permanent sequestration. There are a lot of challenges regarding carbon credits and the eventual fate of mitigated CO_2 depending on the use of produced biomass. However, the enhanced growth of microalgae through indirect BCM could be

a viable option for the reduction of CO_2 emissions from point sources.

3. Options for biological mitigation of CO_2

3.1. The global carbon cycle

According to the recent studies on the geochemical cycle of carbon, the abundance of atmospheric CO_2 over the past $>10^6$ years is regulated by the carbon cycle which includes geological processes such as silicate weathering, carbonate precipitation, carbonate metamorphism, mantle CO_2 degassing, oxidative weathering and burial of organic carbon [30]. The principle "natural" processes that lead to the release of CO_2 to the atmosphere from land and water include, animal and plant respiration, and the decay of vegetation where oxygen and nutrients are converted into CO_2 and energy [31]. Carbon absorbed by vegetation (123 GtC/yr) is stored in biomass, but plant respiration leads to 60 GtC/yr being released back to the atmosphere [31]. The release of CO_2 from currently decaying biomass as well as respiration of plant and animals in the ecosystem leads to a release of a further 60 GtC/yr to the atmosphere. Overall, this results in the sequestration of 3 GtC/yr in soils [11,31,32]. Likewise, in the oceans, photosynthetic organisms absorb 92 GtC/yr while respiration and decay leads to the release of 90 GtC/yr. This leads to a carbon sequestration rate of 2 GtC/yr in the ocean [3,31]. Volcanic eruptions also release carbon from rocks deep in the earth's crust though the amount is relatively small on a global scale [33]. It is estimated that global volcanic CO_2 emissions are approximately 0.13 GtC/yr [34], but this is dwarfed by the estimated 9 GtC/yr emitted through human activities [31]. Human activities have led to an imbalance in the global carbon cycle. As the rate of release of CO_2 exceeds the rate of carbon sequestration, an increase in the concentration of CO_2 in the atmosphere ensues. This increase is estimated at a rate of 4.2 GtC/yr [31,35]. There are a range of sources of CO_2 both natural and anthropogenic leading to the gradual increase in atmospheric carbon. The natural "carbon cycle" includes CO_2 used in plants during photosynthesis and the exchange of CO_2 between the atmosphere and the oceans. The anthropogenic carbon cycle is compiled from CO_2 emissions from human activities such as the burning of fossil fuels and cement production [33]. The annual net increase in atmospheric CO_2 is attributed to the increase in anthropogenic CO_2 emissions from fossil fuels used in transport, energy and industry sectors [31].

3.2. Carbon mitigation pathways

3.2.1. Direct carbon sequestration

Direct carbon sequestration offers the most potential in solving the problems with reducing large scale CO_2 emissions from point sources due to its ability to sequester concentrated CO_2 for extended periods, before it is released to the atmosphere. Before it can be collected and transported to the carbon sink, CO_2 must first be separated from the flue gases. Pre combustion capture of involves the removal of carbon from the fuel through gasification before the fuel is combusted. The produced gas is composed mainly of carbon monoxide and hydrogen and is known as a synthesis gas (syngas) [36]. The carbon monoxide produced is reacted with steam to produce more hydrogen and CO_2 which is removed using the post combustion methods [37]. The produced hydrogen may then be used as fuel for various applications. Oxyfuel combustion is the combustion of fossil fuels in a nearly pure oxygen environment [38]. This process involves the removal of nitrogen from the air before combustion producing the required high oxygen content gas (95% or higher) This produces a flue gas with up to 95% CO_2 which can be easily compressed and transported to storage [38]. Post combustion removal of CO_2 is a more common method of CO_2 removal. There are a variety of methods for post combustion CO_2 removal from the flue gas stream (Fig. 1). The following most commonly used pathways for CO_2 removal have been previous reviewed:

- Absorption [39]
- Membrane separation [36]
- Desiccant adsorption [6]
- Cryogenic Separation [40]

Chemical removal involves the use of amine solvents to absorb the CO_2 from the flue gases. It is the most commonly used approach for CO_2 removal and while the other methods listed above have been considered, they are less energy efficient and more expensive than chemical absorption [6]. The most preferred solvent for chemical removal are amines (monoethanolamine–MEA) [39,41]. The formed compound is easily separated from the other flue gases, and now heat may be used to isolate CO_2 from the compound for compression and transportation [37].

3.2.1.1. Carbon capture and storage. While the focus of this paper is the potential of biological carbon mitigation to sequester

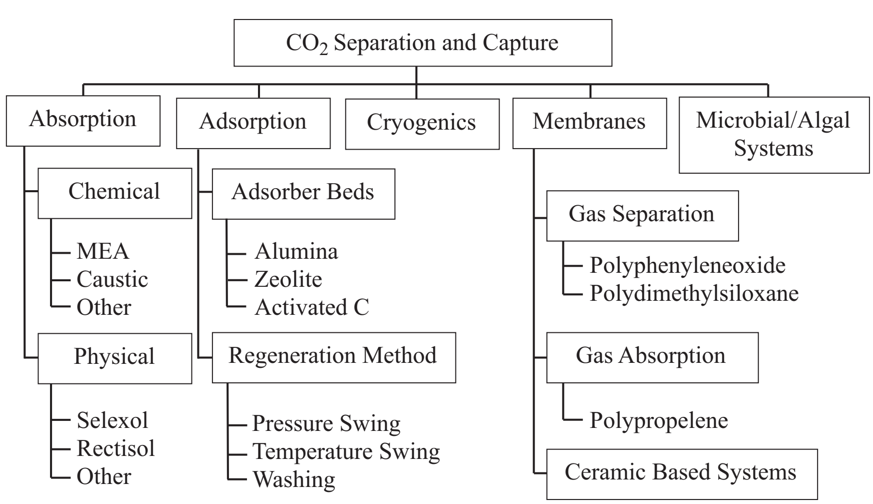


Fig. 1. Technology options for CO_2 separation and capture [41].

carbon from point sources, carbon capture and storage (CCS) is mentioned here to outline current carbon mitigation practises as well as providing an overview of all the pathways currently being used for carbon sequestration. CSS can be defined as the removal of CO_2, which would otherwise be emitted to the atmosphere, directly from the point source of production and subsequently storing it in secure reservoirs [8,42]. The most applicable reservoirs for CSS include depleted oil and gas reservoirs, deep saline formations, and un-mineable coal beds [43]. Geological CSS is often the first choice for carbon storage due to the massive underground capacity and relatively mature injection technology [43]. The main driver for the use of CSS is in its potential to provide emissions cuts sufficient to stabilize greenhouse gas levels, while still allowing for the continued use of fossil fuels [44]. CSS occurs in three stages: capture, transport and storage [37]. Before the CO_2 can be transported and injected into the reservoir, it must first be removed from the flue gases of the point source. In power plants, CO_2 may be isolated before or after combustion and the removal process may be physical or chemical [37]. The process of CO_2 removal is described in detail in Section 5. The separated CO_2 may then be piped or transported in pressurised tanks to the storage location [37]. The storage of CO_2 may occur in a number of formations as described below. Carbon sequestration also has its disadvantages. There is concern that the occurrence of leaks from the reservoirs could result in the release of large volumes of CO_2 [6]. However the biggest challenge with this approach is the added cost of CO_2 separation from the emission streams without any economic gain from the process [45]. Oceanic injection is one method of marine carbon sequestration. There are a number of techniques by which CO_2 is injected into the ocean including droplet plume, dense plume, dry ice, towed pipe injection and CO_2 lake formation [6]. The general methodology is to pump CO_2 into deep waters ($>$ 1000 m) where it is sequestered by the ocean. Techniques include:

- Droplet plume: liquid CO_2 injected from a manifold below 1000 m, forming a rising plume.
- Dense plume: a dense CO_2 seawater mix that sinks, injected at a depth between 500 and 1000 m.
- Dry ice: dropped off a boat and allowed to sink and diffuse.
- Towed pipe: injected from a boat at a depth of 1000 m, forming a rising plume.
- CO_2 lake: injection at a depth of around 4000 m to form a stable "deep lake"[6].

The main setback with ocean injection is the same as that of ocean nourishment where ocean acidification occurs and the waters become inhabitable to wildlife [7]. Also, ocean injection leads to a short term sequestration of carbon with an estimated 15–20% of the CO_2 being leached back into the atmosphere over only a few hundred years [46]. Geologic injection on the other hand involves the injection of CO_2 into geological formations. It has an expected retention rate of thousands of years when compared with only hundreds for oceanic injection [6]. The formation of underground carbonate minerals would prolong the residence time while reducing the risk of escape of CO_2 into the atmosphere [46]. In geological storage, under supercritical conditions, CO_2 is also less dense than water and so will tend to migrate to the top of the storage formation. If the pressure becomes too high, or the formation becomes weakened the highly pressured CO_2 may inevitably leak at some extent causing uncertainties on the storability of the reservoirs [43].

In another form of carbon sequestration, CO_2 is injected into a 70–80% depleted oil well reservoir to enhance recovery of the fuel [37]. Enhanced Oil Recovery (EOR) works on the principle of pressure differential where pressurised CO_2 pushes oils of a density less than 900 kg/m^3 towards production wells. When CO_2 is injected into an oil reservoir, the gas becomes miscible with the oil and promotes movement of the oil through the rock reservoir and out of the wells [6]. Any CO_2 that mixes with the recovered oil is separated at the well and re-injected [37]. Simulations show that EOR can increase production from oil fields by 8–15% of the original oil in place, and that 2.4–3.0 t of CO_2 can be stored for every tonne of oil recovered [37]. Whilst the oil and gas industry has successfully injected CO_2 into reservoirs, to date this has mainly been for increased yield of fossil hydrocarbon reserves and not for long-term storage [45]. Xie et al. [43] outlines the potential problems with EOR including: decreased injectivity due to problems with reservoir compaction, precipitation of minerals, oil emulsification and bacteria growth; uncontrollability of reservoir due to buoyancy forces and leakage; environmental consequences due to leakage into water aquifers and extracting contaminants in solution; as well as energy and financial conflicts due to a balance between cost of CO_2 injection and carbon credits for sequestered carbon. Rather than CSS the main purpose behind this activity has been enhanced recovery of fuel, rather than carbon sequestration [45].

3.2.2. Indirect carbon sequestration

Currently, 55–65% of all anthropogenic CO_2 emissions are removed from the atmosphere by natural sinks [35]. This includes interactions with the ocean as well as photosynthesis in vegetation on the land. Table 1 illustrates the rate of carbon sequestered by the various natural pathways, as well as the total amount of carbon stored in each sink.

3.2.2.1. Terrestrial carbon sink. The soils of the earth contain over 2000 GtC and the vegetation cover helps sequester up to 3 GtC/yr making it a significant natural carbon sink [31]. Carbon sequestered

Table 1
Summary of established direct and indirect carbon sinks.

Carbon sink		Mitigation period	Total carbon content (Gt)	Carbon mitigation (Gt/yr)	Net Carbon sequestration (Gt/yr)	Pathway back to atmosphere	Reference
Soil	Biomass	Short	550	120	0	Plant respiration, microbial decay	[11]
	Soil	Long	2,300	0	2	Carbon sequestered	[10]
Ocean	Biomass, Ocean acidification	Short	1,000	90	0	Air-water exchange, Respiration, decay	[31]
	Deep ocean	Long	37,000	0	2	Carbon sequestered	[31]
CCS	Aquifers	Long	–	200	200	Carbon stored	[46]
	EOR	Long	–	2.4–3t/t oil	–	Carbon stored	[37]
	Biochar	Long	–	0.001	–	Carbon stored	[56]

in living vegetation is estimated at 550 GtC. Therefore long living plants such as trees work as a good carbon sink in the medium term [31]. Terrestrial carbon mitigation may be divided into three groups based on timescale of sequestration. Of the 120 GtC absorbed by photosynthetic organisms, 60 GtC returns to the atmosphere almost immediately via plant respiration [14]. A further 10 GtC is used in plants for growth and maintenance making up the total of 550 GtC sequestered in growing biomass. The rest is shed as litter and enters the soil, where it is decomposed by microorganisms releasing nutrients to the soil and CO_2 to the atmosphere [14,31]. Two GtC/yr remains as organic carbon in the soil indefinitely unless the soil is disturbed [14]. It has been calculated that between 20% and 40% of stored carbon is released after cultivation, most of which is released immediately after such activity [47]. Conversion of forest to agriculture also affects the soil organic carbon stock. Deforestation and conversion to agriculture causes the release of 20–50% of soil carbon to the atmosphere [11]. An increase in atmospheric CO_2 increases the rate of photosynthesis and, provided other resources are readily available, carbon sequestration will increase. However, plant maintenance and soil respiration both increase with temperature, an effect of elevated atmospheric CO_2 levels, thus reducing the carbon mitigation and storage of plants [5]. Peat is also a major terrestrial store of carbon. It is estimated that 20 to 30% of the terrestrial carbon is stored on only 3% of the land area due to peat stores [48]. The total carbon store in northern peatlands is estimated at 4.5 GtC and this carbon stock increases at a rate of 0.96 MtC/yr [12]. A study by Freeman et al. [49] shows that plants in a CO_2 rich atmosphere assimilate much larger amounts of CO_2, which in turn is released into the peat. However, bacteria feed on the carbon breaking down the peaty soil which can then be washed away releasing stored carbon from the bog into streams and rivers [49].

3.2.2.1.1. Energy crops. Land availability is an issue with growing large masses of terrestrial plants with competition between food and fuel so cultivation of these plants on cut away bogs can also to be considered [8,50]. One location where the implementation of this process in Ireland would be in the cutaway bogs of the midlands where over 50,000 ha of cutaway bog exist [50]. There is also a peat fuelled power plant located there, where the produced biomass may be co-fired reducing the need for burning the depleting resources of peat, a natural carbon sink. It would also help the power plant reach targets of co-firing (30% biomass by 2015) set out in the Irish Government White Paper [51]. However, the growth of trees such as Sitka spruce (*Picea sitchensis*) on cutaway bog has shown to have some problems with crop establishment [50]. Studies have shown that just 58% of established trees grew, while only 21% grew satisfactorily [50]. The natural density of peat soil may be higher than optimum for seedling establishment due to many years of compaction from layers of peat above [50]. It therefore may have to be loosened, though excessive loosening may dry out the soil too quickly and disturb plant water uptake. Peat soils are depleted in nutrients such as phosphorus, so this must be applied to the land before planting [50]. They are also susceptible to water logging and therefore must be well drained. This can then lead to leaching of the applied nutrients into watercourses causing eutrophication, thus destruction of flora and fauna downstream [50]. Despite this, C4 plants such as *Miscanthus* and switchgrass have great potential as bioenergy crops, thus carbon mitigation [52]. They can achieve high yields, have relatively low cost production as well as having a low environmental impact even when compared with conventional agricultural crops [52].

3.2.2.1.2. Biochar. The application of biochar to soil is proposed as a novel approach to establish a significant, long-term, sink for atmospheric CO_2 in terrestrial ecosystems [53]. Biochar is charcoal which has been created under anaerobic conditions by low-temperature pyrolysis of biomass [54]. Applying biochar to soils results in long term carbon sequestration, improvement of soil properties and biomass waste management while bio-oil produced by pyrolysis may be used as a renewable energy source [55]. There is a strong link between food insecurity, soil degradation, and climate change however utilising biochar to increase soil organic carbon (SOC) levels improves soil quality and fertility [54]. Feedstocks for pyrolysis include agriculture residues, wood chip, energy crops and grass, organic waste, microalgae, and macroalgae [55,56]. The presence of sufficient organic carbon in soil is of great importance because low levels reduces crop yields, the soil's ability to retain water and applied nutrients as well as its' potential to store CO_2 sequestered by growing biomass [54,56]. Biochar derived from the pyrolysis of algae is seen as more beneficial than from other forms of biomass due to its high nitrogen and phosphorus content which further enhances soil fertility as well as reducing the need for fertilisers on agricultural land [56]. Based on public projections of the use of renewable for energy, biochar will have the capacity to sequester 5.5–9.5 GtC/yr [53]. Despite the many benefits of biochar in carbon sequestration, there are issues with the possible effect of increased microbial activity in soils, the increased requirement for nutrients and water in the soils, as well as possible saturation of the terrestrial carbon sink [54]. The perception of these barriers is of great importance as once biochar has been applied to soil it cannot be removed. Therefore, a full understanding of the long-term effects of the application of biochar to soils needs to be assessed before it becomes a viable, environmentally sustainable option for carbon sequestration [54].

3.2.2.2. Natural oceanic carbon sink. There is approximately 50 times more inorganic carbon in the global ocean than in the atmosphere totalling 38,000 GtC with up to 2 GtC being sequestered per annum [3,31]. The sequestration of carbon in the oceans occurs by two processes. It may occur by the solubility pump; and by photosynthesis. The solubility pump exploits the solubility of CO_2 in water. As carbonates are formed in the water, convection currents and ocean currents transport water highly concentrated with CO_2 into the deep ocean where it remains for long periods of time [57]. Fixated carbon by photosynthetic marine organisms becomes sequestered when the organisms die and sink by vertical flux to the deep ocean where it is remains in the sediment [57]. Biological carbon sequestration in the ocean is limited by the availability of nutrients but there have been various initiatives for the adoption of ocean nourishment as a carbon sequestration scheme where sea waters are enriched with nitrogen or iron as described in Section 3.2.2.3. On a geological timeline of hundreds of thousands of years, carbon is stored in the oceans in the form of Magnesium and Calcium salts. The geochemical reactions responsible were first described by Urey [3,58]

$$CO_2 + CaSiO_3 \leftrightarrow CaCO_3 + SiO_2 \quad (1)$$

$$CO_2 + MgSi \leftrightarrow MgCO_3 + SiO_2 \quad (2)$$

here, $CaSiO_3$ and $MgSiO_3$ represent any generic Ca or Mg silicate produced at high temperatures in the Earth's crust. These are inorganic reactions driven by organic processes in microorganisms such as cyanobacteria and microalgae and in the long term store large amounts of carbon [3]. One such microalgal group are coccolithophores which produce calcium carbonate shells around their cells storing carbon indefinitely long after the population has diminished [59]. A study by Cox et al. [5], states that ocean carbon sequestration will reach a maximum rate of 5 GtC/yr by 2100. This would be due to high CO_2 saturation in sea waters.

Climate change may decrease the solubility of CO_2 in water as higher temperatures reduce solubility thus slowing the ocean's response to emissions [5].

3.2.2.3. Ocean nourishment. Ocean nourishment may be described as a process for stimulating the sequestration of atmospheric CO_2 in the ocean by providing the nutrients needed to enhance the production of phytoplankton [60]. The carbon is thus sequestered and efforts have been made to generate tradable carbon credits from implementation of such a scheme [60,61]. Photosynthetic organisms in the upper ocean have the ability to remove large quantities of CO_2 from the atmosphere [61]. Whether they die, or are consumed by a hierarchy in the food chain, their remains ultimately descends into the deep ocean, taking the sequestered carbon with it. The turbulent diffusion in the near upmost sunlit region of the ocean, where much photosynthesis occurs, ensures there is a constant flux of carbon from the ocean surface [60]. The only limitation to the rate of biological sequestration in the ocean is the availability of nutrients in ocean water [61]. The main disadvantage of ocean fertilisation methods is that it can change plankton structures which can have long term effects on the ocean eco-system. Large quantities of produced organic mass sinking to the bottom of the ocean can trigger the production of methane gas, which would counteract the beneficial effect of carbon fixation [6].

3.2.2.4. Biological carbon mitigation. BCM involves the utilisation of biological media for carbon sequestration. Photosynthetic autotrophic organisms and plants utilise this process of carbon fixation as their food source by converting the CO_2 into organic carbon [9]. Photosynthesis is the process by which green plants use energy from light in the photo-synthetically active radiation range (PAR—wavelength 400–700 nm) to form glucose in their chlorophyll-containing tissues [9,13]. There are two stages in photosynthesis namely the light dependant stage and the light independent stage in which complex reactions occur which can be simplified to the formation of glucose and O_2 from CO_2 and water in the presence of light as shown in Eq. 3 [13]:

$$6H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2 \quad (3)$$

The produced glucose is then converted into starch and cellulose storing the carbon in cells of the plant, thus mitigating the inorganic carbon by creating organic carbon [9]. BCM has been proposed as an environmentally friendly method of removing carbon from the atmosphere, while producing many useful by-products in the process [17]. The produced biomass has numerous applications as discussed in Section 6 from energy production to biochemical generation. The sale of these useful by-products helps off-set the cost of BCM strategies [62]. The process of BCM of emitted CO_2 involves a number of stages as illustrated in Fig. 2. The diagram represents a microalgal culturing system utilising flue gas CO_2 with the input of nutrients and solar energy, through cultivation of microalgae to the production of biofuels and value added by-products [63]. The hot flue gases may be channelled through a cooling system to lower the temperature to the optimal media cultivation temperature. This waste heat can be utilised in the drying of harvested biomass later in the process [45]. Cultivation of media occurs under controlled levels of nutrients, light, temperature and CO_2 concentrations. In this example, the nutrients are sourced from a waste water treatment plant. The algae utilise the nitrogen and phosphorus in waste-water and, with sufficient light conditions, convert the CO_2 into biomass through photosynthesis. The produced biomass is harvested periodically and may then be used in various applications such as co-firing, biofuels, bio chemicals, animal feed and food supplements [45,63]. This method of co-processing creates an efficient, cost effective system where carbon emissions are reduced from the point sources while also minimising nitrogen and phosphorus effluent from the waste water treatment system. The result is an enhanced yield of high value biomass for the various applications as illustrated in Fig. 2 [63].

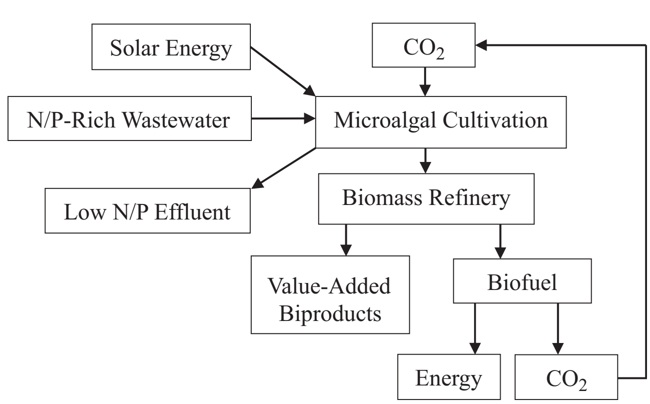


Fig. 2. A conceptual microalgal system for combined biofuels production, CO_2 bio-mitigation, and N/P removal from wastewater [63].

4. Biological media suitable carbon mitigation

4.1. Microalgae

Photosynthesis is the original process that created the fixed carbon present in today's fossil fuels, and microalgae are the origin of these fuels. They are among the fastest growing photosynthetic organisms, using CO_2 as their main building blocks [64]. Although the culturing of microalgae at an industrial scale can be expensive, it has huge potential in producing fuel either from direct combustion, thermochemical or biochemical processes. These include gasification, pyrolysis, liquefaction, and anaerobic digestion (Section 6). Microalgal photosynthesis can also result in the precipitation of calcium carbonate, a potentially long-term sink of carbon [17,65]. There are many advantages associated with utilising microalgae to capture CO_2 from flue gases of power plants. Microalgae are fast growing, with biomass volumes doubling in less than 24 h for most species. For a flow rate of 0.3 l/min of air with 4% CO_2 concentration, a carbon fixation rate of 14.6 g C m^{-2}/day at a growth rate of 30.2 g can be achieved [66]. This makes microalgae very well suited to carbon mitigation, as their high growth rates can keep up with the continuous flow of CO_2 from the power plant (Table 2).

Co-firing is an attractive option for microalgae as is its conversion into biofuels such as biodiesel. Biodiesel is cleaner than petroleum diesel and is virtually free of sulphur, which eliminates the production of sulphur oxides [9]. Microalgal culturing also yields high value commercial products. Sale of these high value products can offset the capital and the operation costs of the process [17]. A cost and energy balance shows that energy production from marine biomass is an attainable target with the currently available technologies. But, in general, the obtained biofuel is too expensive when compared to fossil fuel prices. However, with the introduction of carbon taxes and the ever increasing price of oil, the cost energy balance will become economically favourable while reducing carbon emissions [65]. One of the main challenges with microalgae culturing is the capital cost. The required photobioreactors (PBR) are expensive and so a government grant scheme may

Table 2
Carbon mitigation and growth productivity of selected microalgae.

Strain	Growth temp (°C)	Operation type	Production system	CO_2 Conc. (%)	Growth rate P(g/l/day) (dry weight)	Specific growth rate (μ_{max})	CO_2 removal (g/l//day)	Reference
Botryococcus braunii SI-30	25–30	Batch	PBR	–	1.1	–	1	[129]
Chlorella kessleri	30	Batch	Conical flask PBR	0.038	0.090	0.257	–	[87]
				6	0.087	0.267	–	
				12	0.086	0.267	–	
				18	0.061	0.199	–	
Chlorella sp.	26	Semi-continuous	PBR	2	1.21	0.492	0.261 (58%)	[85]
				5	0.062	0.127	0.316 (27%)	
				10	0.010	n/a[a]	0.466 (20%)	
				15	0.009	n/a	0.573 (16%)	
Chlorella sp.*KR-1*	25	Batch	Jar	10	1.15	–	–	[77]
				30	1	–	–	
Chlorella vulgaris	25	Batch	Tubular PBR	Air	0.4	–	0.075	[130]
Chlorococcum littorale	25	Semi–continuous	Flat plate PBR	5	9.2	–	16.7	[131,132]
		Batch	PBR	20	0.4	1.872	4	[64]
Dunaliella	3	Batch	PBR	27	0.17	–	0.313	[63,133]
Haematococcus pluvialis	16–18	Continuous	Tubular PBR	Air	0.076	0.25	0.143	[95]
Euglena gracilis	27	Semi-continuous	PBR	10	–	0.32×10^6	64.8% 0.4 g	[134]
Monoruphidium minutum	25	Batch	Flask	13.6	1	–	90%	[83,99]
Nannochlorophsis oculata	30	Batch	–	5	–	1.6	–	[90]
			–	8	–	1.6	–	
			–	> 10%	0	0	0	
	26	Batch	–	0.03	0.268	0.194	–	[86]
			–	2	1.277	–	0.211 g/h (47%)	
		Semi- ontinuous	PBR	0	0.480	0.571	–	
				5	0.440	–	0.234 g/h (20%)	
				10	0.398	–	0.35 g/h (15%)	
				15	0.372	–	0.393 g/h (15%)	
Scendesmus obliquus	30	Batch	Tubular PBR	0	0.04	0.15	–	[92]
				6	0.10	0.261	28.08%	
				12	0.14	0.25	13.56%	
Spirulina sp.	30	Batch	Tubular PBR	0	0.14	0.33	–	[92]
				6	0.22	0.27	53.29%	
				12	0.33	0.33	45.61%	

[a] No value—growth was inhibited after 4 days.

be necessary to encourage utilisation of the technology by power plants. Raceway pond production is less expensive to build and operate so may be a more viable solution to the economics of the process. However, it is more difficult to keep cultures axenic in raceway ponds and productivities are much lower than in PBRs [67,68]. In Ireland, poor sunlight may be a problem especially in the winter months. Artificial lighting may then have to be utilised to ensure survival of the microalgal culture but with the consequence of increasing production costs.

4.2. Macroalgae

Like microalgae, macroalgae are autotrophic aquatic plants using inorganic CO_2 as their food source. Microalgae have received greater attention than macroalgae in the past for CO_2 fixation due to their facile adaptability to grow in ponds or bioreactors and the extended knowledge and research of the many strains used for fish feeding [65]. Macroalgae have traditionally been collected from natural basins but in recent times, they have been considered for large scale cultivation and energy production. They have rapid growth rates and like microalgae have many value added by-products. Through gasification energy yields of up to 11,000 MJ/$t_{dryalgae}$ have been achieved compared with 9500 MJ/t for microalgae. The *Gracilaria cornea* (*Rhodophyta*) strain is produced on a large scale for animal feed using commercial CO_2. Using flue gases as a CO_2 source would greatly reduce the cost of production of macroalgae while increasing the biomass yield [69]. Yields of macroalgal species such as *Porphyra yezoensis*, *Gracilaria*sp. *G. chilensis*, and *Hizikia fusiforme* were increased 2–3 times when grown at enhanced levels of CO_2 compared with atmospheric CO_2 cultivation [70]. Using macroalgae for carbon mitigation at power plants will negate the need for using commercial CO_2 thus reducing the cost of biomass production and there are a number of strains which have been adopted for this purpose (Table 3). A study carried out by Israel et al. [69] shows that biomass yield of *Gracilaria cornea* using flue gases was comparable with achieved yields using commercial CO_2. Currently, large scale cultivation of macroalgae is confined mainly to Asia where commercial CO_2 is used to increase the biomass yield. However, in recent times it is being considered elsewhere as its capacity as a valuable resource becomes more apparent across the world. Marine macroalgae have many useful applications in the alginate industry, horticulture, cosmetics, biomedicine and their nutritional value in sea vegetables as well as agricultural fertilisers. Due to technological and financial hindrances commercial production of macroalgae is unviable so traditionally it has been harvested from natural basins. This has an effect on the environment large scale production in the vicinity of a high carbon source may be the solution to lower the cost of production [71]. Production of algae requires balancing the seawater pH with CO_2 and adding essential nutrients, primarily Nitrogen and Phosphorus as in microalgal cultivation. The use of flue gases containing 12 to 15% CO_2 have been found to maintain the desired pH [69]. Macroalgae is very well suited for carbon mitigation due to its high growth rates, satisfactorily utilising CO_2 from the flue gases of the power plant. It has many useful

Table 3
Carbon mitigation and growth productivity of selected macroalgae.

Strain	Growth temp (°C)	Operation type	Production system	CO_2 Conc. in water (%)	Growth rate	Specific growth rate (μ_{max})	CO_2 removal	Reference
Gracilaria Cornea	25	Batch	Tank	12–15	15[a]	–	–	[69]
Porphyra yezoesis	15	Batch	Tank	Air	40[b]	–	–	[135]
				1000[c]	60	–	–	
				1600	100	–	–	
Gracilaria sp.	20	Batch	Cylindrical vessel	345	0.2[d]	–	320[e]	[136]
				1050	0.4	–	891	
				1616	0.6	–	1420	
G. chilensis	20	Batch	Cylindrical vessel	345	0.5	–	292	
				1050	0.7	–	883	
				1616	0.9	–	1280	

[a] Growth rate measured in kg DW/m^2//yr.
[b] Thallus length.
[c] CO_2 concentration measured in ppm.
[d] Growth rate as function of increase in fresh weight of culture.
[e] CO_2 concentration in outlet gas stream (ppm).

Table 4
Carbon mitigation and growth productivity of selected cyanobacteria.

Strain	Growth temp (°C)	Operation type	Production system	CO_2 Conc. (%)	Growth rate (mg/l/d)	Specific growth rate (μ_{max})	CO_2 removal	Reference
Aphanothece microscopica Nageli	35	Batch	PBR	15	–	0.04	109.2[a]	[73]
Chlorogleopsis sp.	50	Batch	PBR	5	–	0.65	20.45[b]	[100]
Fischerella 113	45	Batch	Flask	0.1	0.5	0.8	–	[137]
				0.5	0.5	–	–	

[a] Carbon fixation rate measured in mg/l//h.
[b] Carbon fixation rate measured in mgC/l//d.

applications including as fertiliser for agriculture and human or animal nutrition. It may also be co-fired in the power plant reducing the need for fossil fuels [71].

4.3. Cyanobacteria

Bacteria are fast growing unicellular organisms. Cyanobacteria are photoautotrophic bacteria utilising CO_2 as their food source and are therefore functional in carbon mitigation. They grow in a temperature range of 50 to 75 °C and require anaerobic conditions, light and the absence of N_2 for good growth producing hydrogen as a by-product (Eq. 4) [72]:

$$CO_2 + H_2O + \text{“light energy”} \rightarrow [Cn(H_2O)n] + O_2 \quad (4)$$

Photo heterotrophic bacteria or cyan bacteria can fix N_2 and this reaction is catalysed by the nitrogenase enzyme. This enzyme also catalyses the evolution of H_2 (Eq. 5) [72]

$$N_2 + 8H^+ + 8e^- + 16ATP + \text{“light”} \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi \quad (5)$$

This process may be exploited by utilising selected strains of cyanobacteria for direct biological carbon mitigation applications (Table 4). The biofixation of CO_2 by cyanobacteria in photobioreactors is considered a sustainable strategy, as CO_2 can be incorporated into the molecular structure of bacterial cells in the form of proteins, carbohydrates and lipids. Lipases such as triacylglycerol acylhydrolase are produced, which may then be catalytically synthesised into biodiesel [73]. One strain found to be particularly adept at carbon mitigation is *Synechococcus* and has achieved a CO_2 uptake rate of 0.025 g/l/h or 0.6 g/l/day at a cell mass concentration of 0.286 g/l. If scaling up were plausible, this would equate to a bioreactor of size 4000 m^3 with an average fixation rate of 1 t CO_2/h from emission sources although there could be challenges to overcome. Using *Chlamydomonas reinhardtii*, collection rates of 2 ml/h of hydrogen and 12 ml/h of oxygen were obtained [6,74]. *Rhodovulum sulfidophilum* has been found to have particularly good H_2 production rates. A H_2 evolution rate of 37.5 lmol/200 ml culture after the addition of acetate over a 1 h incubation period was measured for the strain. This hydrogen has many uses including fuel-cell powered cars reducing the need for fossil fuels as well as providing a cheap H_2 production method [6]. Bacteria can be enzymatically broken down into useful products such as biodiesel. Enzymatic synthesis of biodiesel can be carried out either in organic solvents or in solvent-free systems. In biodiesel production the most commonly used catalysts are NaOH, KOH and sodium methoxide. Very significant yields of 99% for the transesterification reaction have been achieved with these catalysts [74]. Despite having excellent growth rates and exceptional productivity, the production of biodiesel from bacteria is quite limited. The lipids produced by bacteria must be refined to ensure efficient transesterification. Glycerol is produced as a by-product and must be removed. Results from extensive studies show that glycerol inactivates the enzymes, which was found to be particular problem in the continuous process [74]. Lipases are also inhibited by the presence of glycerol. To avoid this, a hydrophilic substance such as acetone or silica must be added to the reaction, which will absorb the glycerol, substantially reducing its effect. The formation of other unwanted by-products which reduce biodiesel quality such as soaps, mono- and diacylglycerols, and pigments are also problematic [74]. Although hydrogen is produced by enzymatic synthesis of bacteria, it would not be viable to carry out the

reaction for this purpose alone. From an economic point of view it is much more expensive than chemically synthesised H_2 and this is expected to be the case for decades to come. However, coupling carbon mitigation with hydrogen production and biofuel production, the process could become much more economically feasible [72].

5. CO_2 recovery from point source flue gases for biological carbon mitigation

There are a range of point sources of CO_2 which may be successfully used for the cultivation of biological media (microalgae, macroalgae or cyanobacteria) in biological carbon mitigation schemes. The highest emissions of CO_2 are derived from the combustion of fossil fuels however cement, iron and steel production also account for large proportions of world CO_2 emissions [75]. While these represent the high emitters of CO_2, microalgae may also be grown on flue gases emitted from many other industries which emit significant amounts of CO_2 including the production of petrochemicals, sugar, tyres, carbon black, aluminium, paper, inorganic chemicals, fertilizers, as well as in breweries and mining [75, Oilalgae, 2010 #134]. These point sources emit a range of gases, which fluctuate depending on the fuel and processes involved. Fossil fuelled power plant flue gases typically contain varying levels of CO_2, CO, NO_x, SO_x, N_2, H_2O as well as excess O_2 which was not used in combustion. CO_2 levels vary depending on the fuel being combusted. For a combined cycle gas turbine (CCGT) CO_2 concentration in flue gases is approximately 3–4% while 13–14% is common for a coal-fired power plant and up to 25% for flue gases from cement production [37,39]. Before the CO_2 can be sequestered for CCS it must be removed from the gas stream to purify it. Biological carbon mitigation offers great potential as some strains of microalgae can be directly cultivated using flue gases evading the cost of CO_2 separation [17]. As the generation of CO_2 is inherent in the combustion of fossil fuels, efficient capture of CO_2 from industrial sources is regarded as an important strategy in the reduction of atmospheric CO_2 levels [36]. The removal of CO_2 may occur before or after combustion in a fossil fuelled power plant. As a general rule, the higher the concentration of CO_2 present in the stream, the easier it is to remove it [37]. Both means of CO_2 separation can be expected to reduce overall plant efficiency by 8–12%. Therefore, a conventional coal-fired plant with an efficiency of 35% would have its overall efficiency lowered to 23–27% with the addition of a CCS system [37]. While chemical reaction-based CO_2 mitigation approaches are seen to be energy consuming and expensive, direct biological CO_2 mitigation has been seen as a more attractive option as it can lead to the production of biomass energy [76]. Direct biological carbon mitigation is seen as a valuable option for CO_2 mitigation as plants naturally absorb CO_2 through photosynthesis. Microalgae have many advantages including efficient photosynthesis, rapid growth rates, wide tolerance to extreme environments, and potential for growth in intensive cultures. In theory these advantages promise high performance in the reduction of CO_2 [64]. High purity CO_2 gas is not required for the growth of many strains of microalgae, which reduces the cost of pre-treatment of flue gases [17]. Some combustion products such as NO_x can be effectively used as nutrients for microalgae, the major constituents of which in flue gas are nitric oxide (NO). However, while direct use of flue gas reduces the cost of pre-treatment, it imposes extreme conditions on microalgae, such as high concentrations of CO_2 and many microalgal strains are known to be critically inhibited by air containing only 50 ppm of SO [64,66]. Therefore, CO_2 fixation by microalgae may only be possible with flue gas from liquefied natural gas (LNG) plants which does not contain SO_x or by separating the CO_2 chemically before utilising it for algal culture [77]. The effect of CO_2 concentration and the presence of NO_x or SO_x depend on the strain of microalgae in question.

5.1. Effect of SO_x

Many studies have been carried out to study the effect of toxic compounds on the growth of microalgae [78–80]. These studies have shown that the presence of SO_x greatly inhibits the growth of microalgae. For many strains of microalgae the presence of 50ppm of SO_2 stops growth [81]. SO_2 leads to a reduction in pH in the medium with a concentration of 400 ppm SO_2 reducing the pH to below 4 after just 20 h thus inhibiting the growth of algae [9,82]. However, with the introduction of NaOH to bring it back to pH 8, growth is not inhibited by the presence of SO_x [82]. Therefore it can be considered that it is the effect of pH reduction that reduces growth rather than toxicity of SO_x [82].

5.2. Effect of NO_x

Studies carried out by Yoshihara et al. [80] show that algae can grow effectively while absorbing NO_x during the log phase of growth. However, the addition of NO and NO_2 at the early stages actually inhibited growth [80]. In that study the microalgae (*Nannochlorophsis* sp.) effectively utilised NO_x at concentrations of up to 300 ppm as a nutrient and reduced its presence in the flue gas by 50% [80]. In a similar way to SO_x, the presence of NO_x decreases pH in the media. However, its effect is much less with unaffected growth recorded in NO_x concentrations of up to 240 ppm [9]. The presence of NO in flue gas is oxidised in the presence of oxygen to form NO_2^- in aqueous solution which inhibits the growth of microalgae. The accumulation of NO_2^- is amplified in higher concentrations of O_2 as shown by Matsumoto et al. [82]. This effect can be evaded by changing the nutrient source in the media from $NaNO_3$ to $NaNO_2$. In the case where $NaNO_2$ was used, NO_x had no hindering effects on growth; instead it was used as a nitrogen source for the algae [82,83].

5.3. Effect of CO_2

Many studies have shown that elevated levels of CO_2 in the air stream increases productivity of a range of strains of microalgae [17,63,79,81–91]. However, at high levels of CO_2 (above 20% for many strains) biomass productivity reduced and in some cases ceases though it depends greatly on the cell density of the culture as well as its pH [86]. Some strains such as *Nannochloropsis oculata* grow much more effectively in 2% CO_2 than in air but above 5% CO_2 growth is suppressed [90]. The CO_2 removal efficiency of a particular system depends on the cultivation technique, microlalgal strain, cell density, light intensity, temperature, and the concentration of CO_2 in the air stream [86,92,93]. Many studies have calculated the carbon mitigation rate of CO_2 by selected microalgal strains as described in Section 5.7 which shows the potential of microalgae for BCM. It can be assumed that approximately 2 t of CO_2 is required to produce 1 t of algal biomass [9]. In a study by Chiu et al. [85] *Clorella* sp. was shown to have higher CO_2 removal capacity but lower productivities at low CO_2 concentrations [92,93]. At higher concentrations of CO_2 more carbon was mitigated and biomass productivity was greater, however removal efficiency was lowered due to algal cells utilising the abundant carbon for metabolic activity rather than for making cell organelles [86]. This study showed that the optimum level of carbon mitigation occurred at 1% CO_2 despite other experiments which demonstrate good growth rates at higher concentrations of CO_2 [94]. Taking this into account, the

inlet concentration of CO_2 in the air stream is of great importance in BCM as low levels may lead to poor biomass productivity; while over a strain specific upper limit a loss of CO_2 may occur where the excess which cannot be utilised by the microalgae before it is emitted from the production system [93]. This would lead to large amounts of CO_2 being emitted from the cultivation system, contradicting the efforts of BCM.

5.4. Effect of pH

The effect pH has on growth varies with different strains of microalgae. In general a pH of 7 for freshwater algae and 8 for marine microalgae is the optimum for growth, while at pH below 4 most microalgae cease to grow [9,82,95]. As pH decreases the productivity of the algae also decreases to a point where growth [77]. The presence of CO_2, SO_x, NO_x all affect the pH of the media, the most significant effect on pH being associated with high concentrations of SO_x in flue gases. In general CO_2 is the main mechanism which dictates the pH of the cultivation media [96]. This is because when CO_2 dissolves in sea water it exists in three different inorganic forms namely aqueous carbon dioxide ($CO_{2(aq)}$), bicarbonate (HCO_3) and carbonate ion (CO_3^{2-}) as illustrated in Eq. (1) on equilibrium in the carbonate system[96,97].

$$CO_{2(aq)} + H_2O \leftrightarrows H_2CO_3 \leftrightarrows HCO_3^- + H^+ \leftrightarrows CO_3^{2-} + 2H^+ \quad (6)$$

Increasing the concentration of CO_2 in the media lowers the pH due to the effects of acidification and this has an effect on the physiology of microalgae [98]. Moazami et al. showed that cultures of *S. minor* and *S. cylindricus* grew effectively in pH ranging from 5.0 to 9.5 but with reduced productivity at pH greater than 8.5 [98]. Studies have shown that as the pH increases with biomass concentration, therefore careful management of pH in the early stages of growth are of utmost importance to ensure growth is not inhibited [99]. This may be achieved by the addition of a buffer (i.e., NaOH or CO_2) to bring the pH back to the optimum level for growth of the specific strain of microalgae [82].

5.5. Effect of temperature

Since flue gases from point sources such as power plants have high temperatures (around 120 °C) the use of algae tolerant of high temperatures would achieve significant reductions in cooling costs of the gases [100]. Most microalgal species considered for carbon mitigation are mesophilic microalgae (optimum growth in temperatures of 13–45 °C) with high tolerance to CO_2 while there has also been some studies carried out in the production of thermophilic cyanobacteria (temperatures of 42–75 °C) to address the problem with cooling costs, however, high productivity cannot be achieved with cyanobacteria [100]. Another problem with cultivation of microorganisms at these high temperatures is loss of water through evaporation. Within the mesophilic range, an increase in temperature will lead to an increase in productivity up to a critical temperature limit at which growth is hindered for the specific strain of microalgae [77].

5.6. Effect of soot

There has been limited research carried out on the effect of soot on the growth of microalgae. A study carried out by Matsumoto et al. [82] showed that when the concentration of soot exceeded 0.2 g/l heavy metals were present in amounts (Ni = 1 ppm, V = 0.1 ppm) which impeded growth of microalgae. However, the concentration of soot in flue gases from power plants rarely exceeds 50 mg/m^3 and therefore it does not pose a threat to microalgae productivity [9,82]. If the concentration of soot does become too high for algal cultivation, an electrostatic precipitator (ESP) may be used to collect the ash and heavy metals from the flue gases. ESP's are large electrical devices that electrostatically charge the ash using high voltages which causes it to precipitate out of the flue gas stream [101]. The main components of coal fired flue gas are Al_2O_3 SiO_2 Fe_2 O_3 accounting for 80–90% of fly ash mass. To comply with regulations of flue gas content (50 mg/N m^3) and particle size (<2 μm) ESP with up to 99% removal efficiencies have been developed [101].

5.7. Microalgal strains for carbon bio-mitigation

A number of studies have been carried out on microalgae to exploit their high photosynthetic efficiencies, and high productivities for rapid carbon mitigation on a potentially large scale [9,63,102,103]. In order to determine the viability of BCM using microalgae and optimum growth conditions must be achieved so that carbon mitigation rates and growth rates may be determined [9]. The CO_2 fixation rate is related directly to light utilisation efficiency as well as cell density of microalgae because the higher the density of a culture the more carbon that may be mitigated provided there are sufficient nutrients for growth [85]. Therefore, efficient utilisation of light by microalgae is of utmost importance to ensure high growth rates and maximum carbon mitigation of the system. Suitable strains of microalgae must be sourced with attributes such as high productivities, easy to harvest, ability to be mass cultured as well as producing biomass which has desirable co-products [104]. These attributes are not shared by all microalgae as for example a highly productive strain may also be a poor competitor in a dense mass culture while a robust strain may have low growth rates [104]. Coccolithophores (e.g., *Emiliania huxleyi*) are also considered to be suitable for BCM as they can fix carbon by photosynthesis as well as in calcium carbonate (coccoliths) which makes them an attractive option [105]. Despite this the presence of calcium carbonate has been shown to reduce the pH of sea water and may lead to a reduction the solubility of CO_2 in water thus releasing it to the atmosphere which contradicts their application for BCM. Zeebe et al. demonstrated that the precipitation of 1 mol of $CaCO_3$ results in a reduction in dissolved inorganic carbon of 1 mol and a decrease in total alkalinity of 2 mol. Table 2 illustrates a list of microalgal strains which have been studied for BCM in experimental literature. The temperature at which cultivation is maximised for a given strain has been defined by the authors, while growth rates and CO_2 mitigation rates are monitored to calculate the carbon mitigation potential of the various strains. The specific growth rate (μ/day) of microalgal strains is also displayed in Table 2. This gives a valuable indication of the biomass productivity of the microalgae. As maximum specific growth rate increases, biomass doubling time decreases making cultivation more economically viable [87]. Recently, there has been an attraction of research and development in the area of genetically manipulating microalgal strains for direct BCM and mass culture. Instead of experimenting on an effective strain for direct BCM at lab scale and trying to upscale for mass culture, focus has turned to finding strains in nature which thrive in mass culture, and trying to manipulate these stains so that they can be grown in dense cultures while changing their physiology to increase their productivity while making them easier to harvest [104].

6. Commercial applications of microalgal biomass

Though mitigation of CO_2 from point sources is the primary goal of algal cultivation, algae also have a number of uses in the production of energy, food and chemicals [16]. Once harvested,

the produced algae may be utilised for beneficial use to offset capital, operational, and maintenance of cultivation systems [9]. Microalgal biomass has a number of useful applications and its utilisation can be categorised as follows:

- Energy—direct combustion, hydrogen production or conversion to hydrocarbons for biofuels
- Foods and food supplements—proteins, oils and fats, carbohydrates, sugars, alcohols.
  Chemicals—colorants, perfumes, vitamins, physiologically-active substances [15,106]

Direct combustion (co-firing) offers the cheapest form of energy recovery from biomass as it does not require much post-cultivation processing [16], while the potential production of biochemicals creates high values products to offset the cost of bio-mitigation of anthropogenic CO_2 [62].

6.1. Energy production

Thermal energy may be derived from algal biomass through number of pathways including direct combustion [62]; pyrolysis [107,108]; gasification [107]; anaerobic digestion [109,110]; anaerobic biohydrogen production [111,112]; liquefaction [113,114]; and biochemical conversion [76,112]. While utilising microalgal biomass as a feedstock for co-combustion or thermal processing in energy generation still releases CO_2 back to the atmosphere, there would be an overall reduction in emissions per unit energy in the power plant as the CO_2 is being recycled by the algae producing the extra energy per unit of CO_2 emissions [99]. It can be assumed that CO_2 released during algae co-firing is recycled and is reused by the algae [16]. Essentially the net CO_2 emissions for burning produced algae is zero so the net plant emissions remains the same while the energy output is significantly increased [16].

6.1.1. Biofuels from microalgae

Microalgae can produce lipids, proteins and carbohydrates in large amounts over short periods of time which make them an attractive option for conversion to biofuels for energy [107]. Biodiesel, for example, is much cleaner than petroleum diesel with emissions of hydrocarbons, carbon monoxide and particulates greatly reduced [9]. It is also virtually free of sulphur, thereby eliminating the production of sulphur oxides [9]. Many reports and articles have detailed the advantages of using microalgae for biofuel production in comparison with other available feedstocks [76,112,115–117]. A number of microalgal species have high lipid contents, which may vary from 1–70%, contributing to a high oil yield [115,116]. The produced lipids are chemically similar to common vegetable oils and are therefore a potential source of biodiesel [16,85,116]. One of the biggest advantages of biodiesel is that it can be used in existing diesel engines without modification [118], and it is suitable for blending at any ratio with petroleum diesel [117]. Microalgae may also be biochemically (fermentation [112]) or thermo-chemically (gasification [112]) converted into bioethanol [117]. The production of bioethanol from algae by fermentation involves firstly the conversion of starch to sugars using enzymes, then the conversion of sugars to ethanol by yeast (*Saccharomycess cerevisiae*) [112]. However, CO_2 is released as a by-product of fermentation so must be recycled in microalgae cultivation to reduce emissions [117]. Another attractive option for produced biomass is the production of biogas (biomethane). Biomethane is a product of anaerobic digestion of biomass gas production and consists mainly of methane (55–75%) and CO_2 (25–45%) [117]. Anaerobic digestion of biomass offers a solution to the problem of waste after lipid extraction while producing a gas high in energy for combustion [109,110]. Coupled with biodiesel or bioethanol production, anaerobic digestion offers a solution to waste biomass couples with added energy production [109]. The spent material after anaerobic digestion can then be used as an agricultural fertiliser due to its high nutrient content [117].

6.2. Feed and food supplements

Considerable efforts have been made to promote the application microalgae for use in human food. However, high production costs have limited algae application to small scale, expensive foods [76]. Dried microalgae also has a dark green colour, slightly fishy smell and undesirably powder like consistency which affects the texture of food it is added to thereby limiting its suitability for incorporation into food products on a large scale [119]. In addition to this, the use of microalgae in large scale food applications will be hampered by food safety regulations on human consumption for a long time to come [120]. Despite this microalgae produced from non-point source emitters have been shown to be very nutritionally beneficial and because of their diverse chemical properties, they can act as a dietary supplement due to a high protein or carbohydrate content or be utilised as a natural source of food colorants [119,121]. Some examples of the use of microalgae for food applications include *Chlorella, Spirulina, Arthrospira, Aphanizomenon* and *Nostoc* [120–122]. Microalgae may also be utilised in feed for aquaculture, pets and farm animals [121]. It is estimated that 30% of world production of microalgae is used for animal feed applications [119]. This has been evident mainly in aquaculture where microalgae are utilised in rearing larvae and juvenile fish, both fresh water and marine [76]. Various strains have been utilised as feed in animal and aquaculture including *Isochrysis galbana, Tetraselmis suecica, Scenedesmus, Chlorella, Brachionus, Spirulina, Haematococcus pluvialis, Pavlova, Phaeodactylum, Chaetoceros, Nannochloropsis, Skeletonema and Thalassiosira* [15,76,120,121]. Certain criteria must be met by algae if they are to be considered for animal feed. In general they must be non-toxic, have sufficient biochemical constituents, should be easily digestible, of a suitable size for ingestion as well as being non-toxic [76]. The high presence of these criteria makes them suitable for animal feed. To ensure that animals and aquaculture receives essential dietary requirements, reports have shown that mixing species such as those listed above is required to guarantee that the animal has a balanced diet [121]. However, high cost of production and difficulties in concentrating and storing dried microalgal stocks proves a major set-back in its utilisation in animal feed [121]. In addition to this further research in the area of risk assessment is required for the application of microalgal biomass produced from point source flue gases as a food or feed substance.

6.3. Chemicals and bioactive compounds

Some high value molecules that can be derived from microalgae are fatty acids, polysaccharides, triglycerides, antioxidants, vitamins, pigments and stable isotope biochemicals [76,121]. These compounds have valuable applications in pharmaceuticals, cosmetics and functional foods [76]. Omega-3 fatty acids in microalgae are sourced normally as eicosapentanoic acid (EPA) and decosahexaenoic acid (DHA) [15]. Omega-3 fatty acids are usually sourced in fish oil, however problems have been emerged with unpleasant taste, the risk of build-up of toxins in fish, and poor oxidative stability of fish oil making microalgae a potential source as it is more simplistic and economical [15,121]. Carotenoids, Phycobiliproteins, and chlorophyll are used as pigments in

food and feed production [15,121]. Carotenoids such as β-carotene, astaxanthin, lutein, zeaxanthin, lycopene and bixin are produced commercially for this process [121]. Examples of microalgae containing these pigments include *Dunaliella salina* for β-carotene, and *Haematococcus pluvialis* for astaxanthin. The most important uses of these pigments are as natural food colorants and as additive for animal feed [121]

6.4. Other uses

If commodity chemicals are produced from microalgae rather than conversion to biofuels, CO_2 reductions can be significantly greater because the carbon is sequestered in chemicals' molecules [9,118]. Utilising microalgae in these forms would result in the sequestration of CO_2 for long periods of time [118]. Microalgae have a range of applications in the building sector including its use as an additive for concrete to increase pre-hardening fluidity, or as plastic filler where the carbon becomes sequestered [62]. Harvested biomass may also act as a nutrient rich fertiliser for land application [62]. Historically, macroalgae are used as soil fertilizer in coastal regions all over the world and in the same way microalgae may be used as a biofertiliser [120]. Microalgae produce polymers for particle adherence which assists water storage in soil as well as nitrogen fixing and the production of bioactive compounds which have a beneficial influence on higher plants [120].

7. Challenges associated with direct BCM strategies

While BCM has many advantages in reducing point source emissions, there are some challenges to overcome before the process may be utilised at a large scale for reduction in CO_2 emissions. There are many obstacles to reducing global CO_2 emissions including rapid population growth, increasing energy demand of emerging economies, high CO_2 emissions of industrialised nations, and slow harmonisation of CO_2 reduction measures between countries [2]. With regard to algal culturing, CO_2 utilisation is an issue where poor removal efficiencies lead to a low mitigation rate [67]. Both algal strain selection and production system design are of great importance in order to maximise CO_2 mitigation rates. Open pond systems are more cost efficient than PBRs but it is more difficult to keep cultures axenic in open systems which is of great importance for the value of the produced biomass [67,68]. PBR production is necessary for keeping axenic cultures and minimising loss of CO_2 but much research and development is needed in the area in order for large scale PBRs to be able to mass cultivate microalgae while making efficient use of solar energy [123]. The technical difficulty in cleaning and sterilising PBRs is also an issue which hinders their application in the production of high value pharmaceutical products [68]. Large scale production of microalgae is required to mitigate CO_2 from point sources. Kadam et al. [16] showed that 1000 ha of open pond land area would be required to mitigate the CO_2 emissions from a 50 MW coal fired power plant. Land availability is especially problematic in developed countries where land near point source emitter is at a premium [123]. There are also geographical issues regarding the climate of developed countries where solar radiation and temperatures vary significantly throughout the year [123]. Consequently, while tropical regions are considered more suitable sites for algal cultivation, CO_2 mitigation systems must be located close to the point source to maximise the economic and environmental efficiency of the process. Large scale production of microalgae schemes need to be compiled from careful modelling and life cycle analysis of the overall process [124]. Failure to execute careful assessment of the energy balances and environmental impacts, may result in some proposed schemes for algal production being unsustainable [124].

7.1. Environmental issues

The implementation of a large scale algal production unit may also cause ecological damage with potential leaks of effluent causing eutrophication of surrounding waters. As it is an intensive production of one microalgal strain in dense culture, any interaction with the surrounding environment could potentially see the commercially produced strain dominating wild strains damaging the ecological balance of the area [125]. Despite this, large scale algal cultivation has environmental benefits such as biological treatment of waste water [63]. This also reduces the economic burden of large scale microalgal cultivation as the algae source nitrogen and phosphorus from wastewater instead of using expensive nutrients [63].

8. Economic analysis

The economics of biological carbon mitigation, as well as the economics of production, harvesting, and utilisation of algal biomass has been assessed in a number of articles and reports [9,19,20,102,104,126,127]. There are a number of costs incurred with biological carbon mitigation schemes and microalgal cultivation especially the capital costs associated with plant modifications, infrastructure, cultivation systems (open pond or PBR), land, water treatment (pre- and post-cultivation), gas delivery, diffusers, and harvesting equipment [9,125]. Running costs of such a system include labour, maintenance, inoculum purchase, harvesting and electricity to power the process [125]. However, these costs may be recovered from the sale of harvested biomass for the various applications discussed in Section 6 including co-combustion, biofuels, food, feeds, chemicals and colorants [76]. The process may also be made more economically efficient by integrating waste water facilities for nutrients in microalgal cultivation as well as using waste heat from industrial processes to reduce costs in drying algal biomass [45].

8.1. Cost of algal cultivation

A number of studies have been carried out on cost analysis of the process of large scale algal cultivation and biological carbon mitigation [67,125,128]. In a study carried out by Alabi et al. [125]the various algal production methods were compared for cost analysis. Capital investment per litre volume of each production system was calculated to be US\$52 l^{-1} for raceway pond, US\$2 l^{-1} for fermenter and US\$111 l^{-1} for PBR. Production costs per kilogram of dried biomass was calculated including running costs and labour where results showed fermenter cultivation the cheapest option at US\$1.54 kg^{-1} (biomass), followed by raceway pond at US\$2.66 kg^{-1} (biomass) and the most expensive by a substantial amount was the PBR at US\$7.32 kg^{-1} (biomass) [125]. Monila-Grima et al. [127] carried out a cost analysis on microalgal production in PBR and found that it cost US\$32.16 kg biomass (dry basis), based on a 13% raw material cost and 17% labour cost with depreciation accounting for 34% of yearly expenses. This highlights the high cost of production using closed PBR systems, with which, after over 50 years of development commercial viability of the process as still not been achieved [67]. Despite the high production rates found in PBRs, their use for algal cultivation is limited due to a negative energy balance with energy inputs exceed energy outputs of biomass or extracted lipids [117]. However, much research is being carried out to

maximise the outputs from algal biomass by converting cellulose to liquid biofuels.

8.2. Cost of CO_2 mitigation

The cost of CO_2 mitigation will depend on the productivity of algal biomass, its carbon content, as well as the efficiency of the overall process. In a study carried out by Stewart et al. [6] a carbon uptake rate of 1.5 g/l/day was assumed for *Synechocystis aquatilis*, and under a natural light cycle up to 2.2 kt CO_2/pond/yr could be mitigated in a 4000 m^3 pond. Kadam et al. [128] showed that a 1000 ha open pond system could mitigate 210,000 t/yrCO_2 of the 414,000 t/yrCO_2 generated by a 50 MW coal fired power plant which means that the system achieved a 50% reduction in CO_2 in flue gas emissions [16,128]. Currently carbon sequestration rates in the US cost roughly US\$40 $t^{-1}CO_2$ per tonne of carbon when buried in saline aquifers in contrast with US\$150 $t^{-1}CO_2$ for processes such as amine scrubbers which remover the CO_2 from the flue gases [125]. Conversely, the cost of mitigation using microalgae cultivated in open ponds has been calculated at US\$793 per tonne CO_2 non-inclusive of cost of transportation and burial of produced biomass [125]. This is very cost intensive at almost 20 times the cost of storage in saline aquifers [125]. However, extra revenue may be created through the production of valuable by-products from the produced biomass thus reducing the cost of mitigation (Section 6).

9. Conclusion

Biological carbon mitigation from point sources offers great potential in the amelioration of climate change. BCM using microalgae has many advantages over conventional carbon sequestration methods as the CO_2 is being utilised to produce high value biomass which has a number of applications in energy production, biochemical generation as well as food and fees applications. This is a more desirable method of carbon sequestration compared with geological storage where CO_2 is pumped into aquifers, because even despite the concerns over leaks in the longer term it has a high cost associated with the separation of CO_2 from flue gases without any economic gains from the process. Microalgae have high photosynthetic efficiencies, utilising solar energy to convert CO_2 to organic carbon locking it into their cell organelles. Depending on the application of the produced biomass this carbon may become permanently sequestered. However, even if the biomass were to be co-fired in a fossil fuelled power plant, the CO_2 emissions per unit energy would be significantly reduced as the CO_2 released during algae co-firing is recycled and is reused by the algae. Essentially the net CO_2 emissions for burning produced algae is zero so the net plant emissions remains the same while the energy output is significantly increased. In conclusion there are advantages both environmentally and economically for the utilisation of microalgae in BCM from point sources.

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